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Ab Initio Prediction of the Equilibrium Structure and Vibrational−Rotational Energy Levels of Fluorofulminate

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The molecular parameters of fluorofulminate, FCNO, have been predicted in ab initio calculations using the coupled-cluster method, CCSD(T), and basis sets of double- through quadruple-ζ quality. In contrast to other halofulminates (ClCNO and BrCNO), the equilibrium structure of the FCNO molecule was found to be well bent, with the parameters r_e(FC) = 1.301 Å, r_e(CN) = 1.200 Å, r_e(NO) = 1.199 Å, $\angle_e$(FCN) = 135.1°, and $\angle_e$(CNO) = 162.0°. The height of a barrier to linearity of the FCNO chain was predicted to be 1870 cm^{-1}. The harmonic frequencies and, in particular, FCN bending-rotation energy levels were calculated. To assist in a future analysis of the high-resolution spectra of fluorofulminate, the effective rotational constant B_v was predicted for various states of the FCN bending mode. The determined regular pattern of low-lying energy levels is consistent with that characteristic of a semirigid bent molecule with a moderately anharmonic bending potential energy function.

1. Introduction

The halide (Cl− and Br−) and pseudohalide (NC−) derivatives of fulminic acid, HCNO, have been recently shown both experimentally[1−3] and theoretically[4−6] to be quasilinear. The ClCNO and BrCNO molecules were found to be bent at equilibrium, however, with a small barrier to linearity of the heavy-atom skeleton. The barrier height was determined experimentally[2] to be 167 cm^{-1} for ClCNO and 131 cm^{-1} for BrCNO. On the other hand, the barrier height was predicted at the CCSD(T)/*spdfgh* level of theory[4,5] to be 156 cm^{-1} for ClCNO and 119 cm^{-1} for BrCNO. Although the NCCNO molecule was found[3,6] to be linear at equilibrium, the CCN bending potential energy function appeared to be strongly anharmonic, extraordinarily flat near the minimum. For all of these molecules, the dependence of the effective rotational constant B_v on the quantum numbers of the XCN bending mode (X = Cl, Br, or C) was found[1−6] to be highly nonlinear, thus indicating strong anharmonicity of the XCN bending motion. Using the ab initio calculated XCN bending potential energy functions,[4−6] it was possible to predict the changes ΔB_v due to excitation of the XCN bending mode to remarkably high accuracy. Up to the sixth excited state of the XCN bending mode, the predicted changes ΔB_v coincide with the experimental values[2,3] to within ±1 MHz.[4−6]

To our knowledge, very little indeed is known about the fluorine derivative of fulminic acid, FCNO. Among the species with the composition [C, F, N, and O], only the most stable isomer, fluoroisocyanate, FNCO, was observed experimentally by low-resolution infrared spectroscopy in argon and neon matrixes.[7,8] An attempt to measure the rotational spectrum of fluorofulminate, in analogy to the chlorine and bromine derivatives, failed.[9] Therefore, as demonstrated by the results of previous calculations on ClCNO, BrCNO, and NCCNO,[4−6] state-of-the-art ab initio methods seem to be a valuable alternative for predicting spectroscopic properties of fluorofulminate. In the most advanced ab initio studies[8,10] reported so far in the literature, the FCNO molecule was computed at the MP2/6-31G* level of theory to be planar and bent, being 104 kJ/mol less stable than the FNCO isomer. The barrier to linearity of the FCNO chain was determined[8] by various theoretical approaches to range from 2 to 41 kJ/mol (170−3400 cm^{-1}).

The present study was undertaken with the aim of predicting the spectroscopic properties of fluorofulminate by the ab initio approach and of assisting future experimental studies. Considering excellent agreement between the experimental and theoretical data for the ClCNO, BrCNO, and NCCNO molecules,[1−6] we hope that the results reported here may be a guide to the assignment of vibrational−rotational transitions in the fluorofulminate spectra. The results may also serve as high-level benchmark data for the evaluation of density functional theory (DFT) for molecules of this type.[10]

2. Method of Calculation

The molecular parameters of fluorofulminate were calculated using the coupled-cluster method including single and double excitations and a perturbational correction due to connected triple excitations, CCSD(T).[11−14] The one-particle basis sets used are the correlation-consistent polarized valence basis sets, cc-pVnZ.[15] The quality of the basis sets ranges from double- (n = D) to quadruple-ζ (n = Q). The largest basis set employed, cc-pVQZ, consists of a (12s6p3d2f1g)/[5s4p3d2f1g] set for carbon, nitrogen, oxygen, and fluorine. Some single-point calculations were performed with the still larger quintuple-zeta basis set, cc-pV5Z. Only the spherical harmonic components of polarization d through h functions were used. In the correlation treatment, the 1s-like core orbitals of all of the atoms were excluded from the active space. The calculations were performed using the MOLPRO-2000 package of ab initio programs.[16,17]

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TABLE 1: Equilibrium Molecular Parameters of Fluorofulminate, Determined using the CCSD(T) Method and Various cc-pV*n*Z Basis Sets

	cc-pVDZ	cc-pVTZ	cc-pVQZ
r(FC) (Å)	1.3192	1.3058	1.3025
r(CN) (Å)	1.2308	1.2086	1.2025
r(NO) (Å)	1.2064	1.2027	1.2009
∠(FCN) (deg)	131.67	134.08	134.78
∠(CNO) (deg)	159.01	161.36	161.88
energy + 267 (hartree)	−0.154185	−0.411981	−0.493221

TABLE 2: Molecular Parameters of the Linear Configuration of Fluorofulminate, Determined using the CCSD(T) Method and Various cc-pV*n*Z Basis Sets

	cc-pVDZ	cc-pVTZ	cc-pVQZ
r(FC) (Å)	1.2982	1.2852	1.2816
r(CN) (Å)	1.1704	1.1558	1.1520
r(NO) (Å)	1.2243	1.2219	1.2205
ΔE^a (cm^{-1})	3177	2283	2017

[a] ΔE is the energy difference between the linear and equilibrium structures.

TABLE 3: Harmonic Wavenumbers (ω, in cm^{-1}) of the FCNO Molecule, Determined for the Equilibrium Configuration at the CCSD(T)/cc-pVQZ Level of Theory

symm^a	ω	PED×100^b
A'	2146	62 CN stretch, 28 NO stretch
A'	1440	55 NO stretch, 38 FC stretch
A'	953	52 FC stretch, 38 CN stretch, 15 NO stretch
A'	515	67 CNO bend, 36 FCN bend
A''	397	100 out-of-plane bend
A'	309	68 FCN bend, 33 CNO bend

[a] Symmetry in the C_s point group. [b] The potential energy distribution, only contributions greater then 10 are quoted.

TABLE 4: Optimized Values of the Structural Parameters of Fluorofulminate, Determined for Various Assumed Values of the FCN Angle at the CCSD(T)/cc-pVQZ Level of Theory

∠(FCN)	180	155	145	134.78	125
r(FC) (Å)	1.2816	1.2882	1.2940	1.3025	1.3149
r(CN) (Å)	1.1520	1.1697	1.1847	1.2025	1.2209
r(NO) (Å)	1.2205	1.2117	1.2062	1.2009	1.1960
∠(CNO) (deg)	180	169.25	165.29	161.88	159.48
energy (cm^{-1})^a	0.0	−1047.3	−1700.9	−2017.4	−1593.2

[a] Relative to the energy of the linear configuration.

TABLE 5: $J = |l_5|$ Rotation-Bending Energy Levels (in cm^{-1}) and Changes in the Effective Rotational Constant B_v (in MHz) Due to Excitation of the FCN Bending Mode, v_5, of the FCNO Molecule

$v_5^{l_5}$ (n, k)	energy^a	ΔB_v ^{b}	$v_5^{l_5}$ (n, k)	energy^a	ΔB_v ^{b}
0^0 (0, 0)	0.0	0.0	2^0 (1, 0)	368.6	−6.0
1^1 (0, 1)	7.7	−21.5	3^1 (1, 1)	377.6	−27.0
1^1 (0, 1)	7.7	23.0	3^1 (1, 1)	377.6	17.2
2^2 (0, 2)	30.3	2.8	4^2 (1, 2)	403.9	−1.8
2^2 (0, 2)	30.3	2.9	4^2 (1, 2)	403.9	−1.7
3^3 (0, 3)	67.4	6.3	4^0 (2, 0)	724.7	−14.3
4^4 (0, 4)	118.6	10.8			

[a] The ground-state energy level is calculated to lie 184.8 cm^{-1} above the minimum of the potential energy function. [b] The ground-state effective rotational constant B_0 is calculated to be 4322.4 MHz.

3. Results and Discussion

The calculated equilibrium molecular parameters of fluorofulminate are given in Table 1. For all of the basis sets employed, the equilibrium structure of fluorofulminate was found to be bent, with the trans conformation of the FCNO chain. The calculated total energy and structural parameters appear to be converging with enlargment of the one-particle basis set. To estimate the complete-basis-set (CBS) limit for a molecular parameter, the exponential/Gaussian extrapolation formula[18] was applied. The total energy lowering from the cc-pVQZ to cc-pV5Z basis set calculated in this way is ≈29 mhartrees, whereas that to the infinite basis set is estimated to be ≈46 mhartrees. The extrapolated total energy for the cc-pV5Z basis set was found to be −267.52230 hartrees. For the cc-pVQZ optimized structural parameters, the total energy was actually computed with the cc-pV5Z basis set to be −267.520241 hartrees, just 2.1 mhartrees above the extrapolated value. Likewise, the CBS limit values for the equilibrium structural parameters were estimated to be r_e(FC) = 1.301 Å, r_e(CN) = 1.200 Å, r_e(NO) = 1.199 Å, $\angle_e$(FCN) = 135.1°, and $\angle_e$(CNO) = 162.0°. The calculated bond lengths and valence angles are accurate to about ±0.002 Å and ±0.1°, respectively. The estimated uncertainties are largely due to neglect of the effects of core-valence electron correlation (see Table 2 of ref 6).

The molecular parameters calculated for the linear configuration of fluorofulminate are given in Table 2. The height of a barrier to linearity of the FCNO chain is calculated to be quite large, being by 1 order of magnitude larger than those determined for the ClCNO and BrCNO molecules.[2,4,5] By using the exponential/Gaussian extrapolation formula,[18] the barrier height could be estimated to be 1920 cm^{-1} for the cc-pV5Z basis set and 1870 cm^{-1} at the infinite basis set limit. In fact, using the cc-pV5Z basis set, the barrier height was calculated for the cc-pVQZ optimized structural parameters to be 1930 cm^{-1}. Therefore, it is resonable to assign an uncertainty of about ±30 cm^{-1} to the estimated CBS limit value. In contrast to the ClCNO and BrCNO molecules, which both are apparently quasilinear,[1,2,4,5] fluorofulminate is thus close to the limit of a regular bent molecule.

The calculated harmonic wavenumbers and potential energy distribution of the normal modes of the FCNO molecule are presented in Table 3. The harmonic force field of fluorofulminate was computed with the cc-pVQZ basis set. Except for the out-of-plane mode ν_6, all of the vibrations appeared to be coupled to each other. Therefore, neither of the in-plane normal modes of the FCNO molecule is truly characteristic. In particular, the normal mode ν_5, corresponding to the FCN bending vibration, has a substantial admixture of the CNO bending vibration.

To characterize further the FCN bending potential energy function, it was determined by optimizing the structural parameters of fluorofulminate for various assumed values of the valence angle FCN. Results of the calculations are presented in Table 4. All of the structural parameters are found to vary significantly with the FCN angle, with the CN bond length changing by as much as 0.07 Å for the FCN angle ranging from 180° to 125°. The FCN bending potential energy function was then used to calculate the rotation-bending energy levels by the semirigid-bender approach.[19] The $J = |l_5|$ rotation-bending energy levels of the FCNO molecule are listed in Table 5. The energy levels are labeled by the rotational quantum number J and, in analogy to the previous studies on the ClCNO and BrCNO molecules,[1−5] by the vibrational quantum numbers v_5 and l_5. The quantum numbers v_5 and l_5 describe the doubly degenerate FCN bending vibration of a semirigid linear molecule. Because the FCNO molecule appeared to be far from this limit, the energy levels are also alternatively labeled by the FCN bending (n) and rotational (k) quantum numbers. The quantum numbers n and k can be

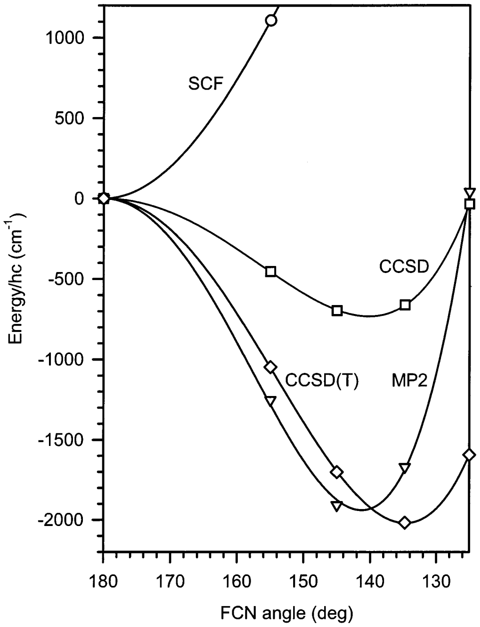

Figure 1. (Relative) total energy of fluorofulminate as a function of the FCN angle, determined using the cc-pVQZ basis set at the SCF, MP2, CCSD, and CCSD(T) levels of theory. The functions are drawn to a common scale.

related[20] to the vibrational quantum numbers v_5 and l_5 by $v_5 = 2n + |k|$ and $l_5 = k$. Then, the calculated rotation-bending energy levels were used to determine the effective rotational constant B_v for each vibrational $v_5^{l_5}$ state. These values were obtained by fitting an odd power series in $(J + 1)$ to the calculated rotational transition frequencies. For the main FCNO isotopomer, the ground-state effective rotational constant B_0 is determined in this way to be 4322.4 MHz. Table 5 lists also the predicted changes in the effective rotational constant B_v due to excitation of the ν_5 mode. The predicted regular pattern of rotation-bending energy levels is consistent with that characteristic of a semirigid bent molecule with a moderately anharmonic bending potential energy function. Moreover, the k dependence of the effective rotational constant B_v is consistent with that characteristic of a near-prolate symmetric top with the rotational constant A of about 230 GHz. This could be expected as the ground FCN bending state lies about 1700 cm^{-1} below the top of a barrier to linearity. The asymmetric-top parameter κ of the FCNO molecule is determined for the equilibrium configuration to be -0.9991. Finally, the parameter γ_0, quantifying quasilinearity of the FCNO chain,[21] is calculated from the rotation-bending energy levels of fluorofulminate to be $+0.92$, as compared with that of $+1$ for an ideal bent molecule. Concerning the quasilinear nature of the FCN bending potential energy function, fluorofulminate resembles thus most closely isocyanic acid, HNCO, ref 22 and references therein.

Figure 1 and Table 6 illustrate the effect of electron correlation on the shape of the FCN bending potential energy function for fluorofulminate. The calculations were performed at various levels of theory, namely, self-consistent field,[23] second-order Møller−Plesset,[24] and coupled-cluster,[11−14] using the cc-pVQZ basis set and the structural parameters given in Table 4. As in the case of the ClCNO and BrCNO molecules,[4,5] fluorofulminate is predicted at the SCF level to be linear at equilibrium, and the primary shape of the FCN bending potential energy function is due to a balance between different electron correlation effects. It is worth noting that the shape of the potential energy function determined at the MP2 level is similar to that determined by the CCSD(T) approach, likely because of fortuitous mutual cancelation of the higher-order correlation corrections to the total energy.

TABLE 6: Total Energy[a] of Fluorofulminate (in cm^{-1}) as a Function of the FCN Angle, Determined using the cc-pVQZ Basis Set at Various Levels of Theory

∠(FCN)	180	155	145	134.78	125
SCF	0	1107.5	1905.7	2703.7	3497.8
MP2	0	−1251.9	−1908.1	−1669.1	41.5
CCSD	0	−452.8	−696.2	−660.4	−34.2
CCSD(T)	0	−1047.3	−1700.9	−2017.4	−1593.2

[a] Relative to the energy of the linear configuration, calculated with the structural parameters given in Table 4.

To estimate intensities of rotational transitions, the electric dipole moment of fluorofulminate was calculated at the CCSD(T)/cc-pVQZ level of theory. For the equilibrium configuration, the dipole moment was determined to be 1.289 D, with the components parallel and perpendicular to the FC bond being 1.181 and 0.516 D, respectively. Using the SCF wave function, the charge distribution was computed by the Mulliken population analysis to be -0.19, $+0.29$, $+0.21$, and -0.31 *e* at the F, C, N, and O atom, respectively.

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